

The University of Chicago

THE HEAT OF DILUTION OF
POTASSIUM CHLORIDE IN AQUEOUS
UREA SOLUTIONS

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1939

By
JOHN F. GALL

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THE HEAT OF DILUTION OF KCl
IN AQUEOUS UREA SOLUTIONS

Introduction

In 1923, Debye and Hückel,¹ by considering the Coulomb forces between the ions in a solution of a strong electrolyte, derived an expression for the variation of activity with concentration. This expression, which becomes asymptotically valid with increasing dilution, gives γ , the mean activity coefficient,² in terms of the dielectric constant, D , of the pure solvent; the ionic valence numbers z_i ; the temperature T ; the individual ionic concentrations C_i ; and the universal constants e , the charge on the electron, the Boltzmann constant k , and the Avogadro number N ; and for a binary electrolyte may be written in the form

$$\log_e \gamma = -\frac{1}{2} \left(\frac{e^2}{DkT} \right)^{3/2} \sqrt{\frac{\pi N}{1000}} \cdot \sqrt{\sum C_i z_i^2} \quad (1)$$

For a uniunivalent electrolyte, this reduces to

$$\log_e \gamma = - \frac{e^2}{(DkT)^{3/2}} \sqrt{\frac{\pi N}{1000}} \cdot \sqrt{2C} \quad (2)$$

where c is now the total (stoichiometric) concentration. From this expression, the relative partial molal heat content $\bar{L}_2$,³ may be obtained by the use of the thermodynamic relation⁴

$$\left(\frac{\partial \log_e \gamma}{\partial T} \right)_p = \frac{-\bar{L}_2}{2RT^2} \quad (3)$$

A quantity which is more convenient for the present work than $\bar{L}_2$ is S , defined in terms of the molality, m , and the apparent

¹Debye and Hückel, Physik. Zeits., **24**, 185 (1923).

²See G. N. Lewis, and M. Randall, "Thermodynamics," The McGraw-Hill Book Co., New York, 1923, p. 328.

³Ibid., p. 88.

⁴Ibid., pp. 279, and 328.

molal heat content ΔH^5 :

$$S = \frac{d\Delta(H)}{d\sqrt{m}} \quad (4)$$

An asymptotic formula, becoming valid in the limit of zero concentration, relates $\bar{L}_2$ and S :

$$\left. \frac{d\bar{L}_2}{d\sqrt{c}} \right]_{c=0} = \frac{3}{2} \left. \frac{d\Delta(H)}{d\sqrt{c}} \right]_{c=0} = \frac{3}{2\sqrt{d}} \left. \frac{d\Delta(H)}{d\sqrt{m}} \right]_{m=0} = \frac{3}{2\sqrt{d}} S^0 \quad (5)$$

wherein d is the density of the pure solvent. These relations are readily derivable from the definitions of the quantities involved.

Equations (2), (3) and (5) may now be combined to give a theoretical expression for the limit, S^0 , of S^6

$$S^0 = - \frac{\sqrt{d}}{D^{3/2} T^{1/2}} \sqrt{\frac{\pi N^3 \epsilon^6}{1000 k}} \left(1 + \frac{T}{D} \frac{dD}{dT} - \frac{1}{3} \frac{T}{d} \frac{dd}{dT} \right) \quad (6)$$

The average value of S between two molalities may be rather directly determined by measuring the heat, ΔH , absorbed when an m_1 molal solution containing n_2 moles of solute is diluted to a molality m_2 . This average value is here denoted by $\bar{P}$, and

$$\bar{P} = \frac{\Delta\Delta(H)}{\Delta\sqrt{m}} = \frac{\Delta H}{m_2 \Delta\sqrt{m}} \quad (7)$$

The derivative S may be computed from the difference quotient $\bar{P}$ by standard analytical or graphical methods. An extrapolation to zero molality will then give an experimental value for S^0 , which may be compared with the theoretical prediction computed according to expression (6). Such a comparison affords, for a given experimental precision, a somewhat more severe test of the theory than does a measurement of the activity coefficient, inasmuch as it requires the theory to be valid over a range of temperature in the neighborhood of the temperature at which the measurements are made.

⁵Ibid., p. 35.

⁶Approximately this equation was first derived by Scatchard, Jour. Amer. Chem. Soc., 53, 2037 (1931), and by Gatty, Phil. Mag., 11, 1082 (1931).

Young and Seligmann⁷ have carried out a careful and objective study of the existing data on the heat of dilution of electrolyte solutions, for the purpose of comparing theoretical and experimental values of S° . They have concluded that excellent agreement exists for salts of 1-1 and 1-2 valence types in aqueous solution.

Only two series of precise heat of dilution measurements have been carried out with dilute solutions of strong electrolytes in solvents other than pure water. These were the measurements by Lange and Robinson⁸ on potassium chloride solutions using aqueous sucrose and urea solutions as solvents. Using Kockel's data⁹ for the dielectric constants of the solvents they computed 532 for the sucrose solution and -228 for the urea solution as the theoretical predictions for S° . Their experimental values were 386 and 332, respectively, in marked disagreement with the theoretical values.

In 1933 more precise determinations of the dielectric constant for urea solutions were carried out by Wyman,¹⁰ who recalculated S° and obtained the value 440. In this computation, however, an arithmetical error was made, and the term involving the thermal expansion of the solvent was neglected.

In view of the uncertainty regarding the correctness of the theoretical predictions in this case, therefore, it was considered advisable to extend the measurements of the heat of dilution of KCl in aqueous urea solutions and to recompute the theoretical values of S° . The measurements also served as a test of the improved calorimeter described below.

Apparatus and Materials

The differential calorimeter used was essentially that constructed by Ronneberg,¹¹ with the substitution of a thermel of con-

⁷Young and Seligmann, Jour. Amer. Chem. Soc., 60, 2379 (1938).

⁸Lange and Robinson, Jour. Amer. Chem. Soc., 52, 4218 (1930).

⁹Kockel, Ann. Physik., 77, 430 (1926).

¹⁰Wyman, Jour. Amer. Chem. Soc., 55, 4116 (1933).

¹¹C. E. Ronneberg, "A Calorimeter For Measuring Very Small Heats of Dilution" (Unpublished Ph.D. dissertation, Dept. of Chemistry, University of Chicago, 1935).

siderably higher sensitivity and several smaller changes noted below. The electrical circuit for measuring the output of the thermel was that used by MacDonald.¹²

The 400 junction thermel which formed the sensitive element of the calorimeter was constructed as shown in Figures 1 and 2. Three 3/16" thick sheets of clear bakelite were fastened together by bakelite screws. Openings cut in the center sheet provided space for the wiring and air spaces for increased thermal insulation. The thermocouple wires, number 34 B. and S. Advance (constantan) and number 21 B. and S. copper (these dimensions being determined by the criteria discussed by Ronneberg),¹³ were threaded through .075" holes in the two outer pieces, as shown. The wiring plan was that shown in the diagram. The crossing of the wires in the upper central part of the thermel resulted in the formation of compensating magnetic loops, which eliminated the possibility of induced currents due to changing external magnetic fields.

The ends of each pair of wires were united by a drop of solder filling the upper half of a small tinned brass eyelet pressed into each hole in the bakelite. These eyelets¹⁴ served the double purpose of providing a rigid support for the couples and preventing the flow of solder very far along the pair of wires. After the junctions were soldered, they were ground to a uniform height above the bakelite of about 1/32". To provide high electrical insulation without excessively reducing thermal contact with the solution, the junctions were next covered with a thin (approximately .03 mm.) sheet of mica, cemented on with Glyptal lacquer,¹⁵ and a sheet of .005" thick gold-plated silver, cemented on with an elastic bakelite cement.¹⁶

The fine wires in the interior of the thermel were protected

¹²J. R. MacDonald, "Heats of Dilution of Hydrochloric Acid" (Unpublished Ph.D. dissertation, Dept. of Chemistry, University of Chicago, 1936).

¹³Ronneberg, op. cit., pp. 9 ff.

¹⁴"No. 1 Silver" eyelets, obtained from the Barrett Binding Co., Chicago, Illinois.

¹⁵Manufactured by the General Electric Company, Schenectady, New York.

¹⁶Obtained from the Bakelite Corporation, Chicago, Illinois.

from corrosion by a coat of Glyptal lacquer, which was introduced through two small holes drilled through the sides of the thermel. The lacquer was dried by a stream of warm air.

The thermel and the two solution vessels were fastened together by means of nickel silver bolts (nickel silver was used because of its low thermal conductivity) and the whole was made watertight by means of a soft hydrocarbon wax.¹⁷ This wax was tested for electrolytic impurities by boiling with conductivity water. No significant change in the specific conductance of the water was observed due to its contact with the wax.

The sensitivity of the thermel, as measured for temperature differences of a few degrees, was about 12,000 microvolts per degree. Taking the thermoelectric power of a single pair of copper-constantan junctions as 40 microvolts per degree, the output of 400 junctions should be 16,000 microvolts per degree. Thus the efficiency of the thermel was about 75 per cent. The departure from 100 per cent efficiency is due to the fact that the junctions are not in direct contact with the solutions, so that the temperature difference between opposite sides of the thermel is somewhat less than the actual temperature difference between the two solutions.

The sensitivity of the Leeds and Northrup high sensitivity galvanometer used in conjunction with the White potentiometer was about 40 millimeters scale deflection per microvolt, so that an EMF of about .01 microvolt could be detected. This corresponded to a temperature sensitivity of about 10^{-6} degrees, corresponding to a change in heat content of about .0005 calories.

A slight modification of the dilution pipette used by Ronneberg was made in order to permit the ground valves to seat independently of each other and of the pull rod. The upper valve was made to fit loosely around the pull rod and was raised by a collar of Monel metal silver soldered to the pull rod and gold plated. The space between the pull rod and the valve was made watertight with wax. A wire link in the pull rod served to make the lower valve seat independently of the upper part of the pull rod. Before the pipette was filled with solution the valves were lubricated with Nujol, a pure paraffin oil.

In order to return the thermel readings to their steady

¹⁷Obtained from the Candy Company, Chicago, Illinois.

state values after a dilution or a calibration heating, a small heater, consisting of a coil of number 40 B. and S. platinum wire wound around a glass tube, was inserted into the reference half of the calorimeter. The resistance of this coil was about 7 ohms, so that a current of .017 ampere produced a temperature rise of about 10^{-6} degrees per second.

In order to make the calibration heating a more automatic procedure, an electric clock switch (constructed by Mr. J. A. Landwehr) was inserted into the circuit controlling the knife switch¹⁸ for closing and opening the heater circuit. Both the clock switch and the pendulum switch described by Groenier were required to be closed before the relay which released the knife switch could operate. The clock switch was therefore adjusted to select the second during which the heating was to be started or stopped, and the pendulum switch then operated the relay at exactly the correct fraction of the second.

The thermostat used for the calorimeter was controlled by a large mercury in Pyrex regulator operating a vacuum tube relay of the type described by Boyd.¹⁹ The temperature remained constant to $.001^{\circ}$ over periods of several days, and, for shorter intervals of time, was subject only to roughly periodic fluctuations of the order of $.0005^{\circ}$ having a period of the order of 30 seconds. A calibrated screw on the mercury regulator provided a ready adjustment ($.0088$ degrees per turn) of the working temperature.

In order to calculate theoretical values of the limit of S, it is necessary to compute the term $\frac{1}{3} \frac{T}{d} \frac{\partial d}{\partial T}$ from measurements of the thermal expansion of the solvent. Sufficient precise data concerning the thermal expansion of urea solutions were lacking; therefore measurements of this quantity were undertaken. Two pyrometers of the type shown in Figure 3 were constructed and used for the purpose.

The volume of each bulb was about 25 c.c., and the capil-

¹⁸W. L. Groenier, "The Heats of Dilution of Sulphuric Acid Solutions" (Unpublished Ph.D. dissertation, Dept. of Chemistry, University of Chicago, 1933).

¹⁹G. Boyd, "Immersion of Some Crystalline Powders in Various Liquids" (Unpublished Ph.D. dissertation, Dept. of Chemistry, University of Chicago, 1937). The circuit is a modification of that designed by Huntner, and Hershberg, J. Ind. Engr. Chem., Anal. Ed., 5, 144 (1933).

lary was about 1 mm. in cross section. The two fiducial marks were engraved about 5 mm. apart, and the position of the meniscus was located with respect to them by means of a telescope with micrometer eyepiece. The measurements were made after thermal equilibrium had been reached in a thermostat constant to within .005 degrees C. A glass counterpoise was used in weighing the pycnometers, and the weights so obtained were reproducible to about .05 milligram. Since about 25 grams of solution were involved, the precision was of the order of 5 parts per million.

The urea used for the heat of dilution experiments and for most of the density measurements was Baker's C. P. Analyzed urea. This was dried at 45°-50° for about 24 hours and cooled over anhydrous calcium chloride. A few density measurements using urea recrystallized twice from water and once from methanol, according to the procedure of Shnidman and Sunier,²⁰ did not give significantly different results.

The potassium chloride used was Malinkrodt's Analytical Reagent, meeting A.C.S. specifications. It was dried twenty-four hours at 110°, and cooled over anhydrous calcium chloride.

All solutions were made up by weight. Those for the density measurements were made with conductivity water; those for the heat of dilution measurements with the laboratory distilled water.

The weights used were calibrated according to the well-known method of Richards. All weighings were reduced to weight in vacuo.

All thermometers were compared with a standard thermometer calibrated by the Bureau of Standards. The Beckmann thermometer used in the thermostat was calibrated twice during the dilution experiments and showed a drift of less than .01° in that time.

Experimental Procedure

The solutions were weighed into the calorimeter at room temperature and were brought to approximately equilibrium temperature by means of heating and cooling devices inserted into the reference half. The heater commonly used was the platinum coil described above. The cooling device used for rough adjustment was a brass tube filled with water which could be frozen. Usually the solutions were cooled to below the equilibrium temperature, and the final adjustments were made with the heaters. The run was always

²⁰Shnidman and Sunier, J. Phys. Chem., 36, 1232 (1932).

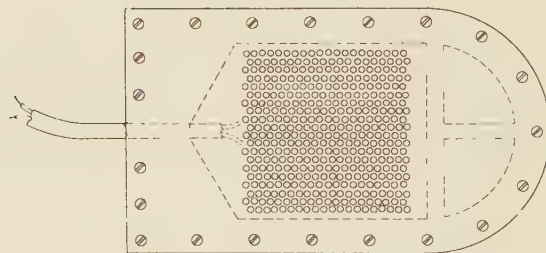


FIGURE 1
Face View of Thermel

To external leads

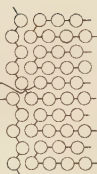


FIGURE 2a
Wiring in Upper Central
Portion of Thermel



FIGURE 2b
Cross-section of Thermel

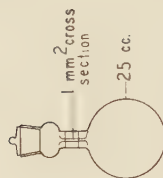


FIGURE 3
Pycnometer

made at least three hours after a steady state appeared to have been reached.

Two readings of the thermel EMF were made each minute, with a check reading of the galvanometer zero between them. Such a program was consistent with a galvanometer period of about 15 seconds. Readings were made for fifteen minutes before, and for twenty minutes after, the dilution and each calibration heating. The heating periods were of two minutes duration, and the current through the heater was adjusted to give a temperature rise of approximately the same magnitude as had occurred during the dilution.

The readings were plotted against time, and the curves extrapolated to the time of opening of the pipette, or to the middle of the heating period, in order to determine the temperature rise which would have occurred if there had been no leakage of heat during the heating interval. The leakage between the two halves, across the thermel, was necessarily rather large (resulting in a drop in the temperature difference of about 4.7 per cent per minute), and the commonly used method of linear extrapolation was of doubtful validity. Accordingly an exponential extrapolator was constructed for the purpose in accordance with the following principles:

If Newton's law of cooling is applicable to the flow of heat across the thermel, the rate at which heat enters one half from the other will be proportional to the difference in temperature of the two solutions. That is, if T_1 and T_2 are the two temperatures, the heat dH_1 flowing into side one in the time dt will be given by

$$dH_1 = k(T_2 - T_1)dt \quad (8)$$

However, a certain amount of heat also appears in each half due to the energy introduced by the stirrers. Designating the heat appearing in unit time due to this cause by S_1 and S_2 , for sides 1 and 2, respectively, and the heat capacities of the two sides as Cp_1 , and Cp_2 , respectively, (8) may be modified to give

$$dH_1 = k(T_2 - T_1)dt + S_1dt = Cp_1dT_1 \quad (9)$$

$$dH_2 = k(T_2 - T_1)dt + S_2dt = Cp_2dT_2$$

or, if $C_{p1} = C_{p2} = C_p$:

$$d(\Delta T) = \frac{1}{C_p} [2k\Delta T + (S_2 - S_1)]dt \quad (10)$$

where $\Delta T = T_2 - T_1$. For a steady state $(S_2 - S_1)$ is independent of time, and (10) may be integrated to give

$$\Delta T = \frac{S_1 - S_2}{2k} + \text{const.} \times e^{-\frac{2k}{C_p} t} \quad (11)$$

For $t = 0$, let $\Delta T = \Delta T^0$; for $t = \infty$, let $\Delta T = \Delta T^{\infty}$. Then, on combining constants (10) becomes

$$\Delta T = \Delta T^{\infty} + (\Delta T^0 - \Delta T^{\infty})e^{-kt} \quad (12)$$

or since thermal readings are proportional to ΔT ,

$$\xi = \xi^{\infty} + (\xi^0 - \xi^{\infty})e^{-kt} \quad (13)$$

The leakage modulus, K , may thus be determined from a plot of $\log_{10} (E - E^{\infty})$ against t , and the relation

$$K = -2.303 \times \text{slope} \quad (14)$$

An approximate value of K was first determined by using temperature differences of the order of a few degrees, in comparison with which ΔT^{∞} was negligible. This was used to compute ξ^{∞} for a series of measurements with ΔT of the order of magnitude encountered in the dilution experiments, and a new and more precise value of K determined. A second approximation was found to leave this value unchanged and equal to .0460 reciprocal minutes.

When $\log (E - E^{\infty})$ was plotted against t , very accurately straight lines were obtained, indicating a close adherence to the exponential cooling law. Accordingly, substituting the value obtained for K in (13) and translating along the E -axis, the function

$$\xi = \xi^0 e^{-.0460t} \quad (15)$$

which is obtained represents very closely the observed cooling curves. This function was plotted on a piece of thin fiber board which was then cut along the curve and used for all of the extrapolations.

It can be shown that the temperature changes so determined will be somewhat higher than would result if no thermal leakage occurred, but the error is approximately proportional to the temperature rise, and, if the method is used for both dilution and calibration runs, will very nearly cancel out. The method has the great

advantage of effectively averaging the readings taken for a considerable length of time (here twenty minutes) after the heating takes place.

The heats of dilution were measured for potassium chloride at 25.00 degrees Centigrade in the concentration range .03 to .16 molal, using aqueous 5 per cent and 15 per cent urea solutions as solvents. Two types of measurements were made with each solvent: For the higher concentrations, "short chords" were obtained by the dilution of a large quantity of solution with the smaller quantity of solvent contained in the pipette; for lower concentrations, the disposition of solvent and solution was reversed; "long chords" being obtained by placing the solution in the pipette, and the solvent outside. The ratio of the volume of liquid outside the pipette to that inside was about 12 to 1.

Density measurements were made of the 5 per cent urea solution at 15°, 20°, 25°, and 30°; and on the 15 per cent urea solution at 15°, 20°, 25°, 30°, and 35°. Each measurement was made in duplicate.

Treatment of Results

The results of the heat of dilution measurements are listed in Tables 1 and 2. Here m_1 and m_2 are the respective molalities (moles per 1000 grams of solvent) of KCl before and after the dilution. ΔH is the heat absorbed during the dilution, corrected for the "heat of opening" of the pipette (see below). $\bar{P}$ is the resultant value of $\frac{\Delta \bar{H}}{\Delta \sqrt{m}}$. Besides these measurements, two test determinations of the heat of dilution of sodium chloride, were made at a concentration of about .1 molal. The values of $\bar{P}$ so obtained were 92.2 and 99.3. These may be compared with $S = 96.0$ and 94.1, respectively, the values computed according to the published equation of Young and Seligmann for NaCl.

Six blank runs, in which the pure solvent was placed both inside and outside the pipette, showed an effective heat of opening of .0019 calorie, with an uncertainty of about .0009 calorie. Probably not all of this represents actual evolution of heat: when the pipette is opened, the stirring conditions change somewhat, and the thermal EMF drifts to a new steady state value in which the working half is cooler with respect to the reference half than before. There is a certain lag, however, before the drift commences,

TABLE 1

HEAT OF DILUTION OF KCl IN AQUEOUS 5% UREA SOLUTION

$\sqrt{m_1}$	$\sqrt{m_2}$	n_2	ΔH Calories	$\bar{P}$
.39740	.38085	.06939	-.0580	50.8
.40008	.33361	.07186	-.0583	48.3
.31702	.30358	.04362	-.0622	106.0
.31702	.30340	.04387	-.06279	105.2
.24962	.23951	.02871	-.0455	156.8
.24962	.23917	.02792	-.0463	159.0
.22227	.21315	.02261	-.0419	203.0
.22227	.21325	.02285	-.0386	186.2
.19823	.19093	.01832	-.0287	214.8
.19722	.18920	.01734	-.0303	217.9
.19722	.19010	.01771	-.0276	218.2
.16965	.04862	.001154	-.0467	334.2
.16965	.04719	.001145	-.0478	341.5
.17364	.05034	.001190	-.0501	342.0
.13288	.03694	.0006975	-.0218	326.2
.13288	.03691	.0006960	-.0216	322.5
.13255	.03708	.0006917	-.0249	377.5

and when the extrapolation to time of opening is made the result is an apparent heat of opening. The measured values of ΔH were therefore corrected by the subtraction of .0019 calories.

As will be shown below, the probable error in $\bar{P}$ increases very rapidly with diminishing molality, and the precision of a long chord is considerably higher than that of a short chord corresponding to the same mean value of $\sqrt{m}$. Consequently, in a graphical extrapolation of a series of long and short chords, it is a matter of difficulty to visualize the proper weighting to be given to the various chords. For this reason an analytical method of extrapolating to zero molality is essential, and the method of least squares as applied by Young and Seligmann²¹ (except for the method of

²¹Young and Seligmann, op. cit.

TABLE 2

HEAT OF DILUTION OF KCl IN AQUEOUS 15% UREA SOLUTION

$\sqrt{m_1}$	$\sqrt{m_2}$	n_2	ΔH Calories	$\bar{P}$
.39214	.37668	.07448	-.1051	91.0
.39215	.37593	.07196	-.1059	90.6
.38990	.37434	.07344	-.1097	96.0
.30952	.29655	.04367	-.0800	141.4
.31180	.29885	.04493	-.0841	144.8
.24049	.23056	.02688	-.0640	196.8
.23979	.22980	.02624	-.0488	190.0
.16884	.16176	.01299	-.0259	281.5
.17123	.16419	.01348	-.0225	237.1
.19408	.05463	.001534	-.0519	242.2
.19853	.05512	.001611	-.0597	258.0
.19853	.05594	.001616	-.0586	254.2
.12717	.03597	.0006614	-.0179	296.5
.12717	.03550	.0006574	-.0156	259.0
.12174	.03431	.0006039	-.0171	324.0

assigning weights) was used here.

If w_p and w_c are the weights of solution or solvent contained in the pipette and working half, respectively, and if R is defined as $\frac{w_c}{(w_c + w_p)}$, the following approximate expressions can

be derived relating $\bar{P}$ and ΔH with the mean value

$$\frac{1}{2} (\sqrt{m_1} - \sqrt{m_2}) = \sqrt{m_c}, \text{ of } \sqrt{m}$$

For a short chord:

$$\bar{P} \approx \frac{\Delta H}{(\sqrt{m_c})^3} \times \frac{1000(1 + \sqrt{R})^3}{8w_c(\sqrt{R} - 1)} \quad (16)$$

For a long chord:

$$\bar{P} = \frac{\Delta H}{(\sqrt{m_c})^3} \times \frac{1000(1 + \sqrt{1 - R})^3}{8w_p(\sqrt{1 - R} - 1)} \quad (17)$$

These formulas will be accurate to within a few per cent

for $\sqrt{m_1}$ less than about .2.

In the apparatus used here, w_p was about 40 grams, and w_c about 460 grams, so that (16) and (17) become:

$$\bar{P} = \frac{49.5 \Delta H}{(\sqrt{m_c})^3} \quad \text{for a short chord} \quad (18)$$

$$\bar{P} = \frac{9.12 \Delta H}{(\sqrt{m_c})^3} \quad \text{for a long chord} \quad (19)$$

An examination of the experimental curves of thermal EMF versus time indicated that for each type of chord there was an approximately constant probable error in the determination of the temperature rise. This amounted to about .0019 calories for short chords and about .0029 calorie for long chords. It was due principally to erratic fluctuations, of uncertain origin and amounting to two or three millionths of a degree, in the temperatures of the solutions. Adding the uncertainty of .0009 calorie in the heat of opening correction gives probable errors of .0028 calorie and .0038 calorie for short and long chords, respectively. By (18) and (19), these will result in a probable error in $\bar{P}$ of

$$\bar{P} = \frac{.138}{(\sqrt{m_c})^3} \quad \text{for short chords} \quad (20)$$

$$\bar{P} = \frac{.035}{(\sqrt{m_c})^3} \quad \text{for long chords} \quad (21)$$

In the reduction of observations by the method of least squares, it is customary to weight the data in proportion to the reciprocal of the squares of the probable errors,²² and to the number, n , of observations, if a given datum is an average of more than one observation. Since the ratio $(.138)^2 / (.035)^2$ is about 15, the weighting factors which might have been used here were nm_c^3 and $15nm_c^3$.

The above discussion, however, has only considered one source of error. Other sources, such as heat loss from the calorimeter as a whole, and errors in determining the initial and final molalities, increase in importance with increasing molality. For this reason, the above weighting factors were softened to nm_c^2 and $15nm_c^2$, for short and long chords, respectively. This was approxi-

²² See M. Merriman, "The Method of Least Squares," J. Wiley and Sons, Inc., New York, 1913, p. 69.

mately the form of weighting factor used by Young and Seligmann.

The values of $\bar{P}$ for solutions of approximately the same initial and final molalities were averaged, and the least squares method applied to these average values. For 5 per cent urea this procedure gave

$$S = 500.7 - 175_{0.6} \sqrt{m} - 152_{5.2} m \quad (22)$$

or $S^0 = 500.7$. For the 15 per cent urea

$$S = 329.2 - 552.9 \sqrt{m} - 168.9 m \quad (23)$$

or $S^0 = 329.2$.

The functions (22) and (23) are plotted in Figure 4 (curves A and B, respectively) together with the averaged values of $\bar{P}$ from which they were computed. On Figure 4 there are also plotted the functions (20) and (21), representing the approximate magnitude of the probable error in the corresponding values of $\bar{P}$.

The measurements made by Lange and Robinson,²³ using 5 per cent urea as solvent, were not included in the determination of the empirical equations. They are undoubtedly of higher precision than the data listed here, but covered too short a concentration range to justify their being combined with the present data. A graphical extrapolation of the chords calculated from Lange and Robinson's data would give a value of S^0 somewhat lower than that obtained here.

The densities of 5 per cent and 15 per cent urea solutions are listed in Table 1. After these measurements were made, the precise data of Gucker, Gage and Moser²⁴ on the densities of urea solutions at 25° and 30° were published. The agreement between the two series of measurements is of the order of .001 per cent.

In order to obtain the temperature coefficients $\frac{d\bar{P}}{dT}$, the difference quotients $\frac{\Delta\bar{P}}{\Delta T}$ were formed and plotted as chords, as in the chord-area method of Young and Vogel.²⁵ At 25°C, the values so obtained for $\frac{d\bar{P}}{dT}$ were .000300 for the 5 per cent urea solution, and, .000393 for the 15 per cent solution.

²³Lange and Robinson, op. cit.

²⁴Gucker, Gage, and Moser, Jour. Am. Chem. Soc., **60**, 2582 (1938).

²⁵Young and Vogel, Jour. Am. Chem. Soc., **54**, 3032 (1932).

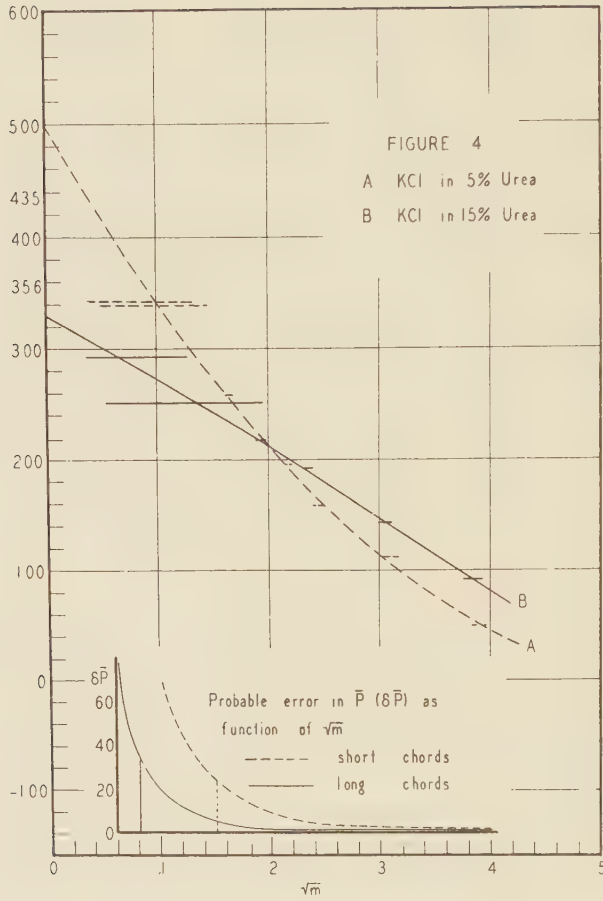


TABLE 3
DENSITY OF AQUEOUS UREA SOLUTIONS

5% Urea		15% Urea	
Temperature °C	Density g./me.	Temperature °C	Density g./me.
15.00	1.0132 ₂₆	14.25	1.041601
	1.0130 ₉₂		1.041541
20.00	1.01189 ₉	19.32	1.03963 ₆
	1.01188 ₆		1.03963 ₄
	1.01187 ₇		
25.00	1.0104 ₈₁	24.83	1.03774 ₈
	1.0107 ₂₉		1.03774 ₈
30.00	1.00882 ₇	29.78	1.93567 ₃
	1.00881 ₈		1.03568 ₇
		34.88	1.0334 ₄₁
			1.0333 ₉₈

An interpolation of Wyman's²⁶ data for the dielectric constants of aqueous urea solutions gives $D = 80.88$ and $\frac{dD}{dT} = -.368$ for 5 per cent solutions; and $D = 85.50$, $\frac{dD}{dT} = -.380$ for 15 per cent solutions. Combining these with the above values for the density, together with Wyman's computation of 1.66116×10^7 for the combined universal constants, gives $S^\circ = 435.0$ and 356.0 , for the 5 per cent and 15 per cent solutions, respectively.

Discussion

It is always somewhat difficult to estimate the precision of an extrapolated value, and this is especially difficult in the present case, where the precision of the data decreases so rapidly in the direction of extrapolation. The probable error of the last chords at the dilute end of the curves is about 20-25 per cent, so that an estimate of 15 per cent for the probable error in S° is not unreasonable. The precision of the theoretical values of S° is

²⁶Wyman, op. cit.

determined largely by the precision of the quantity $\frac{dD}{dT}$. An error of 2 per cent in this coefficient, which is probably a conservative estimate, would lead to an error of about 8 per cent in S^0 .

The discrepancy between the predicted and the experimental values of S^0 for potassium chloride in aqueous 5 per cent urea solution is about 15 per cent (experimental value, 500.7; predicted value, 435.0), and the discrepancy for potassium chloride in aqueous 15 per cent urea solution is about 8 per cent (experimental value, 329.2; predicted value, 356.0). In the light of the above discussion of the magnitudes of the probable errors, it is seen that these discrepancies are not unreasonably large, and that experiment and theory are no longer in definite disagreement for these systems.

The possibility has been suggested that, in the calculation of the theoretical limiting values for the urea solutions, the dielectric constant of the water, rather than that of the solution, should be used.²⁷ The results presented here on 5 per cent urea solutions are not of sufficient precision to decide this point, but those for 15 per cent urea solution seem to indicate definitely that the dielectric constant to be used is that of the solution.²⁸ The results of precise activity measurements in mixed solvents are also in agreement with this conclusion.²⁹

It is interesting to compare the form of the curves obtained here with those for KCl in pure water, obtained by Lange and Leighton. The latter, which may be expressed in the form $S = 477 - 1893 \sqrt{c} - 2144 c$,³⁰ has a steeper initial slope and a greater upward curvature than do the curves for 5 per cent and 15 per cent urea solutions. If the assumption is made that the three

²⁷Lange and Robinson, op. cit.

²⁸It is true that the experimental value of S^0 depends somewhat on the form of equation to which the data are fitted, and that a higher degree curve, possibly sigmoid in form, might give a larger value for S^0 . However, it is unlikely that the result so obtained could in this case be as large as the value, 477, for pure water.

²⁹See for example Harned and Thomas, J.A.C.S., 58, 761 (1936).

³⁰Young and Seligman, op. cit. The difference between c and m in the concentration range considered here is small, and can be neglected for the present discussion.

curves actually approach their corresponding theoretical limits, the three curves will cross in the region $\sqrt{m} = .2$, and there is some indication that they will converge again at higher concentrations. Further measurements at concentrations above $\sqrt{m} = .4$ are needed in order to decide this point.

Summary

(1) An improved differential calorimeter was used in the measurement of the heat of dilution at 25° C. of potassium chloride in aqueous 5 per cent and 15 per cent urea solutions.

(2) The method of least squares was used to reduce the difference quotients $\Delta d(H)/\Delta \sqrt{m}$ (dH = apparent molal heat content) obtained directly from the measurements, to equations giving the derivative $S = d\phi(H)/d\sqrt{m}$ as quadratic functions of $\sqrt{m}$.

(3) Precise measurements were made of the densities of aqueous 5 per cent and 15 per cent urea solutions at several temperatures between 15° C. and 35° C. The results of these measurements were combined with the data of Wyman on the dielectric constants of aqueous urea solutions to give a theoretical value, according to the Debye-Hückel limiting law, of the limit, at zero molality, of S .

(4) It is shown the theoretical and experimental values, so determined, of the limit of S are in reasonable agreement.

